UNLIKE MOLECULAR INTERACTIONS FOR CO_2—N_2 AND A FEW OTHER GAS MIXTURES

H. K. SAHOO AND M. N. SHARMA

DEPARTMENT OF PHYSICS
LUCKNOW UNIVERSITY
LUCKNOW

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ABSTRACT. A study of unlike molecular interaction for gas mixtures composed of several slightly non-spherical molecules and also for mixtures having non-spherical and spherical molecules has been done from the observed temperature dependence of second virial coefficient and thermal diffusion factor, assuming a Lennard-Jones (12 : 6) potential energy function. It has been found that this potential energy function which is strictly applicable to spherical molecules can be applied with success to discuss properties of gas mixtures composed of molecules which deviate slightly from spherical symmetry. Further, the values of the potential parameters indicate the inadequacy of simple combining rules for the case of gas mixtures considered here.

INTRODUCTION

The influence of the law of molecular interaction on properties of gases and gas mixtures is well known and in principle, information about the potential parameters for like and unlike interactions should be obtainable from the experimental determinations of various bulk properties as a function of temperature. Unfortunately, the experimental data for gas mixtures which might lead to a knowledge about the forces between unlike molecules are very meagre. In many cases, the measurements are confined to a single temperature and hence are unsuitable for obtaining any reliable information about intermolecular forces. Thus, generally, for a proper understanding and evaluation of these forces between unlike molecules, use is made of certain empirical combining rules, involving the force parameters of pure components, which have no theoretical justification. Further, these simple combining rules may be valid for central force fields but are certainly not appropriate when we wish to treat molecules like CO_2. Thus, it is very useful and desirable to study the unlike molecular interactions from the temperature variation of properties of gas mixtures wherever such data are available.

For discussing and correlating the different properties of gases and gas mixtures, various formulated expressions for the potential energy function are utilized, such as the Lennard-Jones (12:6) and the modified Buckingham (Exp:6) functions. The (Exp:6) function is said to be more realistic and more flexible, but both of

them had practically the same success in predicting the properties of gases and it is difficult to establish the superiority of one potential over the other as has been concluded by Madan (1955), Mason and Rice (1954) and DeRocco and Halford (1958). However, the (12:6) potential energy function is definitely much simpler and easy to handle and has, therefore, been widely used.

Srivastava and Madan (1953) utilized the temperature variation of thermal diffusion factor for the study of the law of molecular interaction for some gas pairs on the (12:6 model. Later, Srivastava and Srivastava (1957, 1959) and Srivastava (1957) used the properties of interdiffusion and thermal diffusion, mostly of rare gas mixtures, for this purpose on the (Exp:6) model. The assumptions in the theory make both the potential energy functions strictly applicable to spherically symmetric molecules, such as those of monatomic gases at moderate pressures. When the molecules of a gas are not spherically symmetric, there are great mathematical difficulties in discussing their properties rigorously and there is no completely adequate analysis of intermolecular forces between asymmetric polyatomic molecules. However, the theory based on the above mentioned potential energy functions has had success in correlating transport phenomena in polyatomic gases and the assumptions may not be a severe limitation as has been discussed by Chapman and Cowling (1952). It is also seen that rather high asymmetry is required before deviations from the force law applicable to spherical molecules become appreciable. Thus, the same law can be taken to describe the properties of molecules which are slightly non-spherical and for all practical purposes, such derivations will be quite adequate. Further, they will also provide a means of extrapolation and interpolation of the existing data into regions of higher or lower temperatures.

In the present paper, we have used the (12.6) model to study the law of molecular interaction involving unlike molecules and have chosen two sets of binary gas mixtures. The one consisting of mixtures of diatomic gases with a common polyatomic gas such as mixtures of N_2, O_2 and CO with CO_2 of H_2 with BF_3 and the other consisting of a monatomic gas with diatomic gases and also with a polyatomic gas such as mixtures of A with N_2, O_2 and CO_2 and of Kr with N_2. The latter set is interesting since it involves an interaction between spherical and non-spherical molecules.

Recently, Cottrell *et al.* (1956) determined the second virial coefficients of the mixtures of CO_2 with N_2, O_2, CO and A. Grew *et al.* (1954) have reported the experimental data on thermal diffusion of CO_2—N_2, A—N_2, Kr—N_2 and A—O_2 and several other gas mixtures while Raw and Kyle (1956) have reported data on H_2—BF_3 mixtures. We have utilized here both these sets of data for determining the potential parameters. For the gas mixtures chosen, there have been practically no attempts to estimate the potential parameters, in particular, using second virial coefficient and thermal diffusion factor and to correlate the experi-

mental data with the theory based on the Lennard-Jones (12 :6) potential. The thermal diffusion of A—N_2 mixture has, however, been used by Srivastava and Srivastava (1957) for an (Exp:6) model and the diffusion data of CO_2—N_2 and CO_2-O_2 mixtures by Walker and Westenberg (1958, 1960) for a (12:6) and an (Exp: 6) model but an equilibrium property like the second virial coefficient has not been previously used for this purpose. Although the observed data for second virial coefficient are not too extensive in view of the experimental difficulties and limitations of measurement and also as this is the only data available for gas mixtures at more than one temperature (the other measurements are mostly at a single temperature and hence cannot be used in finding the parameters) it is considered worthwhile to examine these data and make the best possible use of them.

THEORY AND FORMULAE

The second virial coefficient B_M, for a gas mixture is given by the relation

$$B_M = x^2{}_1 B_{11} + 2x_1 x_2 B_{12} + x^2{}_2 B_{22} \qquad \ldots (1)$$

where x_1, x_2, B_{11}, B_{22} are the mole fractions and second virial coefficients of components 1 and 2 and B_{12} is the interaction second virial coefficient having a direct relation to the law of unlike molecular interaction through the reduced second virial coefficient B^* given by Hirschfelder, Curtiss and Bird (1954)

as $$B_{12} = b_{12} B_{12}^*(T^*)$$

where $$b_{12} = \frac{2\pi}{3} N r_{12}^3 \text{ and } T^* = KT/\epsilon_{12} \qquad \ldots (2)$$

The parameters ϵ_{12} and r_{12} are the depth of the potential well and the separation distance for zero potential energy for unlike molecular interaction.

The general expression for thermal diffusion factor is quite complicated and moreover, different theoretical expressions are available for this quantiy such as those of Chapman and of Kihara. Kihara's expressions are much simpler than the corresponding ones of Chapman and are more accurate as has been observed by Srivastava (1957) and many others and have therefore been used here. $[\alpha_T]_1$, Kihara's first approximation formula for thermal diffusion factor may be written in the convenient form

$$[\alpha_T]_1 = (6C^* - 5)g \qquad \ldots (3)$$

where g is a complicated expression involving molecular weights, composition and collision integrals for which reference can be made to Srivastava (1957).

The principal contribution towards temperature dependence of thermal diffusion factor comes through the factor $(6C^*-5)$ which involves only unlike interactions. The factor g depends only slightly on temperature. This slight

variation hardly shows any definite trend and is itself liable to uncertainties on account of various errors as has been observed by Srivastava and Madan (1953). Further, even if this variation is considered and is taken account of, as has been done by Srivastava and Srivastava (1957) and Srivastava (1957), the results do not show any appreciable variation, the deviations being well within the limits which result from considerations of the effect of the error in the experimental measurements. Thus $[\alpha_T]_1$ varying as $(6C^*-5)$ is quite reasonable for all paractical purposes.

DETERMINATION OF POTENTIAL PARAMETERS

The methods of determining the potential parameters from the experimental data have been discussed recently by Srivastava and Srivastava (1959), Whalley and Schneider (1955) and Strehlow (1953) and others. They mainly consist of (1) graphical ratio method used successfully by Srivastava and Madan (1953), Madan (1955), (1957), Sharma and Madan (1960) and Bunde (1955); (2) the translational method of Keesom (1912) and Lennard-Jones (1924); (3) the intersection method of Buckingham (1938). The translational method requires data over a large temperature range and unless there are some distinguishable peculiarities in the curve as has been discussed by Srivastava and Srivastava (1957). a multitude of translations is possible and the method fails. The intersection method requires accurate data for only a few temperatures which need not extend over a large temperature interval but the data must be highly accurate, otherwise it is impossible to determine the intersection point. Thus, for most cases, the first method, that is, the graphical ratio method, is quite adequate and suitable for examining and reducing the experimental data appropriately and deducing the potential parameters therefrom. The method is described in detail by Srivastava and Madan (1953), Sharma and Madan (1960) and Madan (1955) and a reference to these can be made.

Usually experimental B_{12} is obtained from B_M by using the calculated values of B_{11} and B_{22} utilizing the values of the force parameters obtained from other measurements which is not a very desirable procedure. To determine the parameters between unlike molecules, we have resorted to purely experimental data, that is, to get B_{12} (experimental), experimentally observed values of B_{11} and B_{22} have been utilized. The values of ϵ_{12}/k and r_{12} determined from the temperature dependence of second virial coefficient are reported in Table I, together with the temperature ranges for which they have been calculated. The potential parameters obtained from temperature dependence of thermal diffusion factor are given in Table II(a) & II(b). Using ϵ_{12}/k, the value of r_{12} has been calculated from experimental interdiffusion coefficient wherever such data are available. The potential parameters thus obtained from second virial coefficient and thermal diffusion factor are compared with other determinations including those obtained with the help of the combining rule viz., $\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}$ and $r_{12} = \frac{1}{2}(r_{11}+r_{22})$

where ϵ_{11}, ϵ_{22} and r_{11}, r_{22} are respectively the depths of the potential wells and the sepa ration distances for zero potential for (1:1) and (2:2) like interactions. These are reported in Tables III and IV.

DISCUSSION OF RESULTS

It will be quite interesting to see how far the potential parameters, obtained by us, agree with those derived from other sources and how satisfactorily these parameters can predict another bulk property. The comparison of parameters has been done in Table III and IV from which it can be seen that the parameters obtained by us are different from those derived using combining rules. The values of ϵ_{12}/k are higher and those of r_{12} are lower than the corresponding combining rule values except for Kr—N_2. A similar trend was noticed by Barua (1959). This is to be expected as the combining rule for r_{12} is true only for molecules which behave as rigid spheres.

The system CO_2—N_2 is interesting because parameters for this could be determined from both second virial coefficient and the thermal diffusion. The combining rule gives a value 134 for ϵ_{12}/k whereas the second virial coefficient gives an indication that this value is $>>134$ and is about 168. This indication is further confirmed by evaluation of parameters from thermal diffusion factor, which is a more sensitive property and the value obtained is 157.1. This is in agreement with the value obtained by Walker and Westenberg (1958) from the temperature dependence of mutual diffusion. The parameters obtained from equilibrium and non-equilibrium properties are also seen to be different as has also been noticed in general by Hirschfelder *et al.* (1954) and Madan (1955, 1957).

Using the different parameters, we could, for comparison, compute the values of coefficient of interdiffusion, another property for which some data are available for these mixtures. This has been done in Table V. However, in general, the parameters derived from equilibrium properties should not be used for calculation of non-equilibrium properties or vice versa because different properties emphasize the potential energy curves differently and cannot be simply correlated. When we take two similar molecules, for example, two polyatomic molecules, we get a reasonably good agreement, but when we have a mixture of a polyatomic molecule with a simple molecule, the agreement is not satisfactory. The agreement between the theoretical and experimental values is good for CO_2—N_2 and CO_2- O_2 (rather it is better than that obtained by using parameters from combining rules) but not for CO_2—CO and CO_2—A. In the latter case, for example of CO_2—A, the interaction is between a spherical and a non-spherical molecule. As expected (Srivastava and Srivastava 1959) due to the non-spherical nature of CO_2 molecule, the potential parameters calculated from second virial coefficient (equilibrium property) do not reproduce the coefficient of mutual diffusion (non-equilibrium property) satisfactorily. In this type of mixture, it seems that the effect of the non-spherical nature of the molecule predominates over that of the spherical

one, even though we can ascribe part of the discrepancy due to possible experi mental errors in the measurement of the coefficient of mutual diffusion for this mixture for which there are the data of only one experimenter at a single temperature. This was obtained by Waldmann from a study of diffusion thermo-effec and is subject to much error as has been discussed by Chapman and Cowling (1952). Further, for this mixture, the thermal diffusion factor, a property very sensitive to the force law, increases with decrease of temperature, a peculiar yet unexplained behaviour, and it is not surprising that a good agreement is not obtained in this case.

The case of CO_2—CO mixture is different. Here, the interaction is between a symmetrical molecule CO_2 with an asymmetrical molecule CO, unlike the interactions of CO_2—N_2 or CO_2—O_2 in which there are symmetrical molecules like N_2 or O_2. Furthermore, the data on second virial coefficient for CO_2—CO mixture shows practically no variation with temperature in the range 30°C to 60°C and an average curve had to be drawn for the determination of potential parameters which are suject to some uncertainty on this account.

In general, for all the gas mixtures, the non-spherical nature of the molecules does manifest itself and it is not surprising that a single set of parameters fails to give same degree of agreement for two different properties and also over a wide temperature range. For CO_2—N_2 mixture, we find good agreement for the coefficient of mutual diffusion, but if the same parameters are used to compute the thermal conductivity, the agreement is not so good as has been reported by Brokaw (1959) and also computed by us and it necessitates the use of a different set of potential parameters for this purpose, even though the discrepancy may also be on account of the complex nature of the phenomenon of thermal conductivity for these molecules.

Unfortunately, for the gas pairs considered here, suitable and extensive data for different properties do not exist and as such, a detailed comparison with experiment is not possible. To arrive at any definite conclusions, it is very desirable to have more experimental data of various properties at different temperatures.

Nevertheless, the analysis is still useful and valid to a good approximation and is definitely of much interest in the absence of sufficient information about the forces between unlike molecules. The evaluation of the potential parameters from the experimental data for the study of forces between unlike slightly non-spherical molecules and the bulk properties of their mixtures, is definitely a better approach than the derivation of these parameters from simple combining rules which are semi-empirical in nature and may be valid only for central force fields.

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TABLE I

Values of potential parameters from second virial coefficient

Gas pair	CO_2 - N_2		CO_2—A		CO_2—O_2		CO_2—CO	
Temperature range (°K)	ε_{12}/k (°K)	r_{12} (Å)	ε_{12}/k (°K)	r_{12} (Å)	ε_{12}/k (°K)	r_{12} (Å)	ε_{12}/k (°K)	r_{12} (Å)
290 – 348	166.8	3.560	156.1	3.426	150 3	3.682	179.8	3.272
300 - 360	169.3	3.516	157 4	3.409	176 5	3.217	179.1	3.281
310 - 372	170.6	3.492	158.7	3.383	---	—	181.3	3.255
Mean	168.9	3.523	157.4	3.406	163 4	3.449	180.1	3.269

TABLE II*a*

Values of potential parameters from thermal diffusion

Gas pair Temperature range (°K)	CO_2 N_2 ε_{12}/k(°K)	A - N_2 ε_{12}/k(°K)	A - O_2 ε_{12}/k(°K)	Kr - N_2 ε_{12}/k(°K)
125 – 250	---	-	—	113.8
150 300	—	112.0	121 9	114.5
175 – 350	—	111.5	115.1	109.4
200 – 400	—	109.9	119.0	104.2
225 – 450	—	108.7	122.9	103.7
250 – 500	178 0	104.2	126.9	105.5
275 – 550	164.7	—	- -	110.5
300 – 600	154.6	- -	—	111.1
325 – 650	147.7	—	—	115.8
350 – 700	142.3	—	—	119.0
Mean	157.1	109.2	121.2	110.7
r_{12}(Å)	3.557	3.428	3.309	—

TABLE II*b*

	H_2—BF_3.	
Temperature range (°K)	ε_{12}/k(°K)	Mean ε_{12}/k(°K)
340 – 408	104.3	
350 – 420	98.3	98.9
360 – 432	94.2	

TABLE III

Comparison of potential parameters obtained from second virial coefficient with those determined from other sources

Gas pair	$\varepsilon_{12}/k(°K)$			r_{12}(Å)		
	(*)	(a)	(b)	(*)	(a)	(b)
CO_2-N_2	168.9	132	134.1	3.523	3.839	4.095
CO_2-A	157.4	153	150.5	3.406	3.707	3.948
$CO_2—O_2$	163.4	147	149.4	3.449	3.715	3.975
CO_2-CO	180.1	145	137.6	3.269	3.793	4.125

(*) Present work
(a) Combining rule, individual parameters from viscosity. Hirschfelder, Curtiss and Bird (1954).
(b) Combining rule, individual parameters from second virial coefficient. Cottrell *et al.* (1956)

TABLE IV

Comparison of potential parameters obtained from thermal diffusion with those determined from other sources.

Gas pair	ε_{12}/k(°K)				r_{12}(Å)			
	(*)	(**)	(a)	(b)	(*)	(**)	(a)	(b)
CO_2-N_2	157.1	168.9	157	132	3.557	3.523	3.516	3.839
$A-N_2$	109.2	-	—	106	3.428	—	—	3.550
$A-O_2$	121.2	—	—	118	3.309	—	—	3.426
$Kr-N_2$	110.7	—	—	132				
H_2-BF_3	98.9	—	—	80.37				

(*) From thermal diffusion (present work)
(**) From second virial coefficient (present work)
(a) Walker and Westenberg (1958)
(b) Hirschfelder, Curtiss and Bird (1954). Combining rule and individual parameters from viscosity.

TABLE V

Comparison of calculated and experimental values of interdiffusion

Gas mixture	Temperature (°K)	(*) D_{12} Cm^2/Sec	(a) D_{12} Cm^2/Sec	experimeztal $D_{12}cm^2/Sec.$(b
CO_2—N_2	273.2	0.141	0.130	0.144
	288.2	0.156	0.143	0.158
	293.2	0.161	0.147	0.160
	298.2	0.166	0.152	0.165(c)
				0.167(d)
				0.168(e)
CO_2—A	293.2	0.159	0.136	0.140
CO_2—O_2	273.2	0.143	0.128	0.139
				0.137(f)
	293.2	0.163	0.146	0.160
				0.153(f)
CO_2—CO	273.2	0.163	0.128	0.137

(*) Present work, paramenters are given in Table I.

(a) Calculated using combining rules, individual parameters from viscosity. Hirschfelder, Curtiss and Bird (1954).

(b) Data taken from Hirschfelder, Curtiss and Bird (1954) unless stated otherwise.

(c) Boyd *et al.* (1951)

(d) Walker and Westenburg (1958).

(e) Boardman and Wild (1937)

(f) Walker and Westenburg (1960)

REFERENCES

Barua, A. K., 1959, *Ind. J. Phys.*, **33**, 221.

Boardman, L. E. and Wild, N. E., 1937, *Proc. Roy. Soc. (London)*, *A***162**, 511.

Boyd, C.A. 1951, *J. Chem. Phys.*, **19**, 548.

Brokaw, R. S., 1959, *J. Chem. Phys.*, **31**, 571.

Buckingham, R. A., 1938, *Proc. Roy. Soc. (London)*, A **168**, 264.

Bunde, R. E., 1955, University of Wisconsin, C.M-850, August.

Chapman, S. and Cowling, T.G., 1952, The Mathematical Theory of Non-Uniform Gases (Cambridge University Press, New York)

Cottrell, T. L., Hamilton, R.A., and Taubinger, R.P., 1956, *Trans. Faraday Soc.*, **52**, 1310.

De Rocco, A.G., and Halford, J.O., 1958, *J. Chem. Phys.* **28**, 1152.

Grew, K.E., Johnson, F.A. and Neal, W.E.J., 1954, *Proc. Roy, Soc. (London)* A **224**, 513.

Hirschfelder, J.O., Curtiss, C.F., and Bird, R.B., 1954, Molecular Theory of Gases and Liquids (John Wiley & Sons, New York).

Keesom, W.H., 1912, Leiden Comm. Suppl. No. 25.
Lennard-Jones, J.E., 1924, *Proc. Roy. Soc.* (*London*), A**106**, 463.
Madan, M.P., 1955, *J. Chem. Phys.*, **23**, 763.
Madan, M.P., 1957, *J. Chem. Phys.*, **27**, 113.
Mason, E.A. and Rice, W.E., 1954, *J. Chem. Phys.*, **22**, 843.
Raw, C.J.G., and Kyle, E., 1956, *Trans. Faraday Soc.*, **52**, 1216.
Sharma, M.N., and Madan, M.P., 1960, *Proc. Nat. Inst. Sci.*, **26**A, 49.
Srivastava, B.N., and Madan, M.P., 1953, *Proc. Phys. Soc.* (*London*) A**66**, 277.
Srivastava, B.N., and Srivastava, K.P., 1957, *Physica*, **23**, 103.
Srivastava, B.N., and Srivastava, K.P., 1959, *J. Chem. Phys.* **30**, 984.
Srivastava, K. P., 1957, *J. Chem. Phys.*, **26**, 579.
Strehlow, R. A., 1953, *J. Chem. Phys.*, **21**, 2101.
Walker, R. E., and Westenberg, A. A., 1958, *J. Chem. Phys.*, **29**, 1139.
Walker, R. E., and Westenberg, A. A., 1960, *J. Chem Phys.*, **32**, 436.
Whalley, E., and Schneider, W. G., 1955, *J. Chem. Phys.*, **23**, 1644.